A STUDY OF ADSORPTION PHENOMENA IN THE VICINITY OF

THE CRITICAL TEMPERATURE

DISSERTATION

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TABLE OF CONTENTS

Acknowledgement

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The investigations to be described are a continuation of
the studies which have been made in recent years by Dr. W. A.
Patrick and his students upon the adsorption of gases and vapors
by silica gel. Anderson[1], working in Zsigmondy's laboratory,
and Van Bemmelen[2] at an earlier date, contributed valuable in-
formation regarding the adsorption by the gel from solutions,
and Patrick[3], while a student at Goettingen, was the pioneer
worker in the field of gaseous adsorption. Under his guid-
ance this work has been resumed in this laboratory, and the
adsorptive powers of the gel have been studied by McGavack[4]
with sulphur dioxide, by Davidheiser[5] with ammonia, by Long[6]
with butane; and by Opdycke[7] with the vapors of alcohol, ben-
zene, carbon tetrachloride and water, using a dynamic method
as contrasted with the static method of the other workers.
The rigorous study of the adsorption of these substances with
improved methods and increased accuracy has thrown much light

1. Anderson, Inaugural Dissertation, Goettingen, 1914
2. Van Bemmelen, Zeit. anorg. Chem. 13, 233 (1896)
3. W. A. Patrick, Inaugural Dissertation, Goettingen, 1914
4. McGavack & Patrick, J. Am. Chem. Soc. 42, 946 (1920)
5. Davidheiser & Patrick, J. Am. Chem. Soc. 44, 1 (1922)
6. J. S. Long, Dissertation, J. H. U., 1922
7. L. M. Opdycke, Dissertation, J. H. U., 1922

on the field, disproving many of the older ideas upon the subject, and answering questions hitherto puzzling.

The strong adsorption of the acidic gas, sulphur dioxide, the basic ammonia, and the neutral butane by the chemically inert silica gel seems to disprove any specific chemical reaction in this adsorption process. That the presence of moisture in the gel plays an important and often a troublesome part was shown by Davidheiser[1], who, using the extremely soluble gas ammonia, found that the volume adsorbed at 0°C. by one gram of gel at a pressure of one cm. of mercury decreased from 82.40 cc. to 28.76 cc. when the water content of the gel was reduced from 4.88% to 0.33%. Thus driving off the water from the gel decreases its adsorptive powers, due to lessening the amount of gas actually dissolved in the water, or to alterations in the gel structure as a result of the drying, or to both. With SO_2 and NH_3, after correcting for the amounts actually dissolved in the water, there remained considerable volumes of the gases truly adsorbed and readily comparable, and Long[2], using the insoluble butane, proved conclusively that the structure of the gel is not destroyed by drying, even tho the pore size, shape and distribution may undergo change. The following table taken from his data illustrates the effect of

1. Davidheiser & Patrick - loc. cit.
2. J. J. Long - loc. cit.

varying the water content upon the adsorptive powers of the
gel. The values of X/M give the number of cc. of gas taken
up by one gram of the gel at 30°C. and 600 mm. pressure.

% of H_2O in the Gel	X/M
0.03	40.5
0.77	41.2
1.96	43.0
3.57	41.0
5.77	40.0

Long points out that, of the gels he used, the sample
containing 1.96% of H_2O seems to possess the maximum activity
and capacity; that increasing the water content brings about
both a decrease in activity and in capacity of the gel, while
a decrease in water content to 0.77% apparently affects only
the capacity. Anhydrous gel shows a slight decrease in both
properties, but in every case the change is so small as to in-
dicate only minor structural changes, and not complete de-
struction as was formerly thought.

That the adsorption is strictly reversible was proven by
McGavack[1], who showed that the hysteresis noted by earlier
workers was fallacious; that identical results can be obtained

1. McGavack & Patrick- Loc. cit.

upon filling and emptying the pores provided the gel has been previously completely freed from adsorbed air and other permanent gases. Failure to work with air-free gel, varying the water content, and the use of non-homogeneous gel samples probably account for many previously noted anomalies in the behavior of the gel.

The experimental results are satisfactorily related by Freundlich's well-known adsorption equation:

$$X/M = \alpha \ P^{\frac{1}{n}}$$

but this expression fails to enable us to predict what the adsorption at one temperature will be, if we know the adsorption at some other temperature. Considering the role of the adsorbent to be merely that of an inert porous body, the formula

$$V = K(P^{\sigma}/P_0)^{\frac{1}{n}}$$

has been shown to interpret the facts excellently in every case. V represents the volume in liquid form of the gas adsorbed, P the equilibrium pressure, P_0 the vapor pressure and σ the surface tension of the liquid at the given temperature, and K and $1/n$ are constants dependent only on the physical structure of the adsorbent. The process of adsorption is then envisioned as a condensation of the gas in the fine pores of the adsorbent,

this condensation being brought about by the capillary forces
which become active when the radius of the pore becomes suf-
ficiently small. With different porous adsorbents, or with
different samples of the same adsorbent, there may thus be
different adsorptive powers, due to dissimilarity in the size,
shape, distribution, internal area and volume of the pores, re-
sulting perhaps from differences in methods of preparation,
drying, heating, etc.: but with any given sample, of fixed con-
stitution and structure, the work indicates that the same vol-
ume of the condensed phase is taken up, regardless of the gas
used, provided the equilibrium pressure be such that the quan-
tity P'/P_0 have the same value, i.e. at "corresponding pres-
sures". From the measurements of one adsorption isotherm and
with a knowledge of such physical constants as surface tension,
density and vapor pressure of the condensed gas, the values of
K and $1/n$ may be readily determined. Furthermore, inasmuch as
these two constants are related only to the structure of the
adsorbent, with a given adsorbent and a knowledge of K and $1/n$
we are in position to calculate the extent of the adsorption
at any pressure and temperature. In other words the available
internal volume of the gel, the pore-space capable of being
filled by capillary action, is a quantity related to the gas
adsorbed only in so far as the ease of the condensation of the
latter determines which parts of the pores become filled, i.e.

which parts have a radius sufficiently small to enable the capillary forces to cause condensation.

The above statements must be qualified to some extent on account of certain factors, the operation of which may be qualitatively understood, but which have not yet been reduced to a quantitative basis. A qualitative view of these effects may be obtained from consideration of a very simple case.
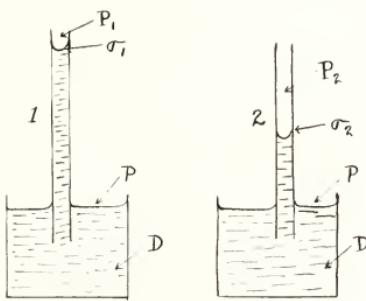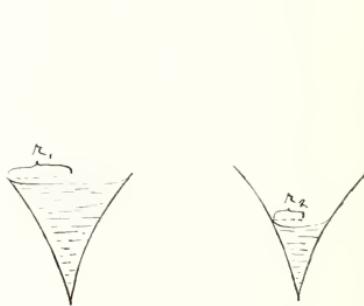
Fig A   Fig B

Suppose two capillaries, 1 and 2 in Fig. A, having the same diameter, be immersed in two hypothetical liquids which have the same density and vapor pressure, D and P, but let the surface tension σ_1 , be greater than σ_2 . Then the liquid will rise to a higher level in capillary 1 than in capillary 2, and since the vapor pressure at the plane surface of each liquid in the reservoir is the same, it follows that the pressure P_1 in capillary 1 is less than P_2 in capillary 2. Then

if the whole system be inclosed in a container and the pressure of the system be gradually increased, it is evident that condensation of the liquid in capillary 1 will commence before a sufficiently high pressure is reached in capillary 2 to cause any condensation. In other words, the capillary forces are more effective in causing condensation in the case of liquids of high than of low surface tension.

The same idea can be applied to condensation in the pores of the gel, which we represent in Fig. B as being conical. Let r be the radius of the pore at the position of the meniscus when the pore is partially filled with the condensed phase. Suppose 1 and 2 represent pores filled with the same two liquids as above, each, of course, being assumed to wet the walls, and therefore to give a meniscus concave upwards. In each case, then, the surface, which tends to contract, will exert an upward pull on the liquid below, tending to draw it up and dilate it. Each liquid will therefore tend to expand and become less dense, but since σ_1 is greater than σ_2, the tendency in pore 1 will be more marked than in pore 2, and as a result, for a given mass of liquid, the volume occupied in pore 1 will be greater than that in pore 2, and the radius of the pore at the meniscus in 1 will be larger than that at the meniscus in 2. So the radius of capillary activity is larger in case 1 than in case 2, leading again to the same conclusion as above, that

the capillary effects are more marked in the case of liquids of high surface tension, and that the liquid in a pore is less dense the higher the surface tension.

These facts, the mathematical formulation from a theoretical standpoint being unknown, undoubtedly explain some of the difficulty encountered when we try to apply values of K and $1/n$ obtained from data on one gas to the adsorption of a different gas. Another disturbing feature was pointed out by McGavack to be the variation in compressibility of the liquid as the temperature rises. In general, the higher the surface tension of a liquid, the lower will be its compressibility. So with different liquids, having different values of σ , we expect different compressibilities; also with the same liquid, the higher the temperature, the more compressible it becomes. Since the vapor pressure of a liquid in a capillary is lowered, and since there is the dilation effect mentioned above, it is evident that this variation is compressibility will have an effect upon the value of V in the equation $V = K(P\sigma/P_0)^{1/n}$, and in lieu of any more exact method of evaluating this effect, it must be included in the constants K and $1/n$. This is offered as a partial explanation of the difference in the values of the constants obtained in the work on sulphur dioxide, ammonia, butane and in the present work on carbon dioxide, altho of probably much greater im-

portance is the variation in the gel samples used. When these errors are corrected, it is believed that the above formula will enable accurate predictions to be made of the amounts of any gas to be taken up by a uniform sample of the gel, provided the physical constants of the gas are known. The accuracy with which the formula is applicable to all of the work so far done seems to justify this belief.

This, in brief, is the capillary theory of adsorption by silica gel and other inert porous adsorbents as developed in this laboratory up to the present time. Since this view involves condensation of a gas to the liquid phase, it becomes of interest to study the case of adsorption in the neighborhood of temperatures at which, under oridnary conditions, no condensation could occur, namely near the critical temperature. Inasmuch as adsorption does occur even above the critical temperature, it is obvious that the capillary theory of adsorption must undergo modification in order to account for such results. By this statement we do not mean to imply that all cases of adsorption are due to capillary forces, but rather that it is possible to extend the temperature range of capillary adsorption above the critical temperature in certain cases. The purpose of the following investigation is, therefore, to modify the present theory of capillary adsorption so as to extend its range above the critical temperature.

Of the gases previously studied, sulphur dioxide has a critical temperature of 157.2°C., ammonia of 132.3° and butane of 153.2°, all temperatures so high as to render difficult a study of adsorption in their vicinity. Carbon dioxide, however, with a critical temperature of 31.1°, easy of preparation, stable, not acting on mercury, not excessively soluble in water, and with physical constants well worked out, seemed ideal for the study and was, therefore, chosen.

MATERIALS USED.

Great care was exercised to obtain samples of gel as pure and uniform as possible. Sodium silicate from Muth Bros. & Co. was mixed with C.P. hydrochloric acid from the J. T. Baker Chemical Co. according to the method described in detail by Long[1]. The sol set to a gel within a few hours and in the gel form was washed continuously for seventeen days, using running tap water. No trace of electrolyte could be found in the wash-water at the end of this time - or for many days before the washing was discontinued. The thoroly washed gel was air-dried on a frame for eleven days, and then refluxed with aqua regia for fifteen hours. It was then washed by decantation with distilled water for ten days, changing the water three times a day, the water appearing pure when tested again for the chloride ion. After drying in air, it was subjected to drying in an electric furnace in a current of air dried by P_2O_5, the temperature being raised but slowly. After thirty-five hours at a maximum temperature of $400°C.$, the gel was ground in a mortar and only that portion used which passed thru a #10 mesh sieve and not thru a #30 mesh. It was then reheated for twelve hours at $550°$, after which time duplicate analyses showed a water content of 3.63% and 3.64%. The sample of this water content was designated Gel A_1. Gel A_2 was heated for two weeks longer at a temperature of $700°$ to $750°$, and subsequent analysis,

1. Loc. cit.

after treatment in the adsorption apparatus, showed a much
lower water content. An analysis of Gel A, was also made
for acid content by heating the gel in a hard glass tube
over Bunsen burners to the softening point of the glass,
while drawing over the gel a slow current of air, which was
then bubbled thru two wash-bottles containing standardized
NaOH. Titration then showed that no acid had been driven off,
and the gel was therefore considered acid-free.

The CO_2 was generated as needed in a Kipp generator which
was rendered as nearly air-free as possible. The marble used
was completely covered with water and boiled for one hour,
then rapidly introduced into the generator and the latter fill-
ed with a solution of one part C.P. HCl and two parts of dis-
tilled water. A small amount of cupric chloride was added to
prevent the evolution of H_2S from any pyrite in the marble.
The gas generated was then passed thru water to remove acid
fumes, thru a mercury trap, and then thru drying tubes of
$CaCl_2$ and P_2O_5 .

All mercury used was purified by filtering thru silk,
washing with 8% HNO_3, then with distilled water and drying
for three hours at 120°.

-13-

METHOD OF PROCEDURE

This has been rather fully described by the previous workers in the field. The volume of gas was measured to within 0.01 cc., pressure to within 0.03 mm., and the temperature of the bath was kept constant to within 0.05°. Evacuation was effected by means of a Cenco Hyvac pump, giving 0.001 mm. pressure, connected in series with a Gaede mercury pump which gave 0.00001 mm., this pressure being too small to register on the MacLeod Gauge used. Before a run was started the gel was weighed out carefully into the adsorption bulb and this was attached by means of a mercury sealed ground-glass joint to the completely evacuated apparatus. The pumps were started and the stopcock turned which opened the adsorption bulb to the system. An electric furnace was then fitted around the adsorption bulb, and during the course of thirteen minutes the temperature was raised to 315°, and was maintained between 315° and 320° for two and one half hours in order to remove all traces of adsorbed gas from the gel. Evacuation was always continued until the MacLeod Gauge registered no pressure. During the early part of the work, in order not to alter the water content of the gel, great care was exercised to duplicate exactly the conditions of this heating and evacuation preliminary to making a run, but later it was found that this was not essential, both in view of the limited solubility of

CO_2 in the extremely small amount of water present, and because a temperature of only $320°$ would have a negligible effect on any water that had remained in the gel after heating to $700°$ to $750°$ for two weeks. However, the temperature regulation was adhered to as strictly as possible, altho the duration of the evacuation was not always the same in the later runs.

EXPERIMENTAL RESULTS

A number of preliminary runs were made at 30° both with Gel A_1 and with Gel A_2 without success. Smooth adsorption curves were obtained, but the curves did not coincide, altho all lay very close together. The smoothness of the curves, their regularity and similarity seemed to indicate that the experimental technique was not at fault, and that the failure to check was due to non-uniformity of the gel samples used, despite the uniformity of the treatment to which they had all been subjected. A close examination of Gel A_2 bore out this view. Most of the gel particles appeared perfectly clear, like glass, but an occasional particle could be seen which was opaque, like china. This might well be explained when we consider the drying of the gel in the electric furnace, where the gel was contained in a quartz tube of nearly one inch diameter. Under a current of air it is readily conceivable that the temperature of the gel near one end might not be the same as that at the center where the thermocouple junction was placed, or near the other end; and also, the gel along the central axis would not be so hot as that actually touching the heated walls of the quartz tube. This latter condition we take to be the chief cause of the non-homogeneity of the gel samples, the actual cell structure of the gel particles in contact with the quartz tube having probably been altered, and the opaque appearance re-

sulting, since very high heat always produces this effect.

To avoid this trouble it was decided to use the same
sample thruout the investigation, rather than to change it for
each run. In this way we know that we have an absolutely def-
inite adsorbent, and so avoid the uncertainty which often be-
clouds adsorption experiments. The preliminary treatment of
the sample was always the same as that described above for the
removal of adsorbed air, the only difference being that we were
now driving off adsorbed CO_2. After the adoption of this method
no difficulty was experienced in making almost perfect dupli-
cate runs, the points obtained in two different runs at the
same temperature lying on a single smooth curve with only very
few and negligible deviations.

The experimental results of the adsorption experiments at
0°, 20°, 30° and 40° are given in Table I. The value of the
water content of the gel (1.28%) is that which actually existed
after the heating and evacuating in the adsorption bulb, so
that any loss of water by this treatment was taken care of.
It is extremely doubtful that there was any appreciable loss
or any structural change in the gel, as the temperature of the
bulb containing the gel was never raised above 320°, while the
gel had been heated to 700° to 750° in a current of dry air
for two weeks in process of preparation. It is unlikely, there-
fore, that the low temperature would drive off water or cause

changes in structure upon which the high temperature had had
no effect. The analysis was carried out by noting the loss
in weight of the sample after blasting in a platinum crucible.
This water content of 1.28% is so small that we may neglect
entirely the solution of the gas in the water. Since the
sample used in most of the runs weighed 1.0526 g. it contain-
ed 0.0135 g. of water. At 20° this would dissolve .012 cc.
of CO_2, which is hardly above the limit of accuracy with which
the volumes could be read from the calibration curve of the
burette. Even this small amount would be lessened, due to the
fact that atmospheric pressure was never reached in the bulb.
Evidently any volume change due to the loss of water by heat-
ing in the adsorption bulb would therefore be infinitely small.

In the following table,

V_0 = total number of cc. of gas introduced, reduced
to standard conditions.

V_1 = number of cc. remaining after the adsorption
was completed, similarly corrected.

X = number of cc. adsorbed ($X = V_0 - V_1$)

X/M = number of cc. adsorbed per gram of gel

P = the equilibrium pressure of the system, ex-
pressed in mm. of mercury corrected to 0°.

TABLE I

Run No. 11

Temp. 0°; Gel A_2; Wt. of sample, 1.1380 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	log X/M	log P
8.44	4.61	3.83	3.37	182.11	0.52706	2.26033
12.89	7.22	5.67	4.98	285.14	0.69744	2.45506
17.24	9.80	7.44	6.54	387.19	0.81543	2.58793
22.05	12.83	9.22	8.10	506.63	0.90859	2.70469
27.52	16.21	11.31	9.44	640.01	0.99732	2.80619

Run No. 12

Temp. 0°; Gel A_2; Wt. of sample, 1.1380 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	log X/M	log P
3.42	1.77	1.65	1.45	68.82	0.16134	1.84398
6.97	3.80	3.17	2.79	149.88	0.44492	2.17574
11.81	6.58	5.23	4.60	259.78	0.66236	2.41461
17.90	10.22	7.68	6.75	403.60	0.82922	2.60595
23.84	13.95	9.89	8.69	550.69	0.93906	2.74091
26.49	15.57	10.92	9.60	614.84	0.98208	2.78876

Run No. 13

Temp. 20°; Gel A_2; Wt. of sample, 1.1580 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	log X/M	log P
2.27	1.56	.71	0.62	61.28	$\bar{1}$.79512	1.78732
5.94	4.15	1.79	1.57	162.81	0.19671	2.21168
10.63	7.57	3.06	2.69	297.32	0.42958	2.47322
16.05	11.63	4.42	3.88	456.64	0.58928	2.65958
21.68	15.90	5.78	5.08	624.23	0.70579	2.79534

Run No. 14

Temp. 20°; Gel A_2; Wt. of sample, 1.1580 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	log X/M	log P
3.60	2.55	1.05	.92	100.24	$\bar{1}$.96505	2.00104
8.59	6.12	2.47	2.17	240.23	0.33656	2.38062
14.77	10.65	4.12	3.62	418.28	0.55676	2.62147
19.87	14.45	5.42	4.76	567.44	0.67786	2.75392
22.88	16.78	6.10	5.36	658.91	0.72919	2.81883

Run No. 10

Temp. 30°; Gel A_2; Wt. of sample, 1.0526 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	log X/M	log P
2.50	1.70	0.60	0.57	69.32	$\bar{1}.75588$	1.84086
6.64	5.12	1.52	1.44	206.36	0.15957	2.31882
11.15	8.72	2.43	2.31	354.66	0.36334	2.54981
16.35	12.91	3.44	3.27	525.13	0.51429	2.72026
19.50	15.38	4.12	3.91	625.93	0.59263	2.79652

Run No. 8

Temp. 40°; Gel A_2; Wt. of sample, 1.0526 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	log X/M	log P
1.72	1.43	0.29	0.28	59.86	$\bar{1}.44013$	1.77714
5.82	4.65	1.17	1.11	194.68	0.04592	2.28932
9.31	7.43	1.88	1.79	311.13	0.25189	2.49294
13.54	11.02	2.52	2.39	461.34	0.37913	2.66402
17.37	14.18	3.19	3.03	593.77	0.48152	2.77362

Run No. 9

Temp. 40°; Gel A_o; Wt. of sample, 1.0525 g.; H_2O content, 1.28%

V_o	V_1	X	X/M	P	$\log X/M$	$\log P$
2.97	2.32	0.65	0.62	97.29	$\bar{1}$.79064	1.98807
7.61	6.14	1.47	1.40	257.12	0.14505	2.41013
12.02	9.76	2.26	2.15	408.82	0.33184	2.61153
15.99	13.14	2.85	2.71	549.99	0.43257	2.74035
18.27	14.94	3.33	3.16	625.44	0.50017	2.79619

Fig. I

Fig II

Runs 11 + 12 at 0°

Runs 13 + 14 at 20°

Run 10 at 30°

Runs 8 + 9 at 40°

Log X/M

Log P
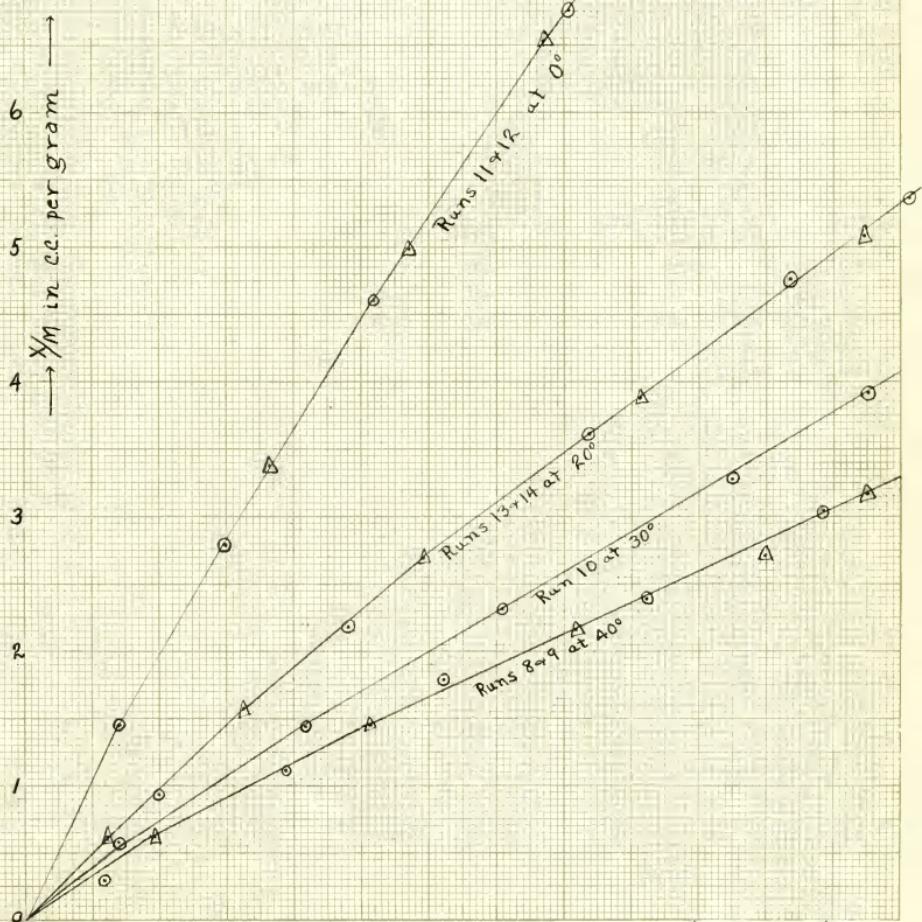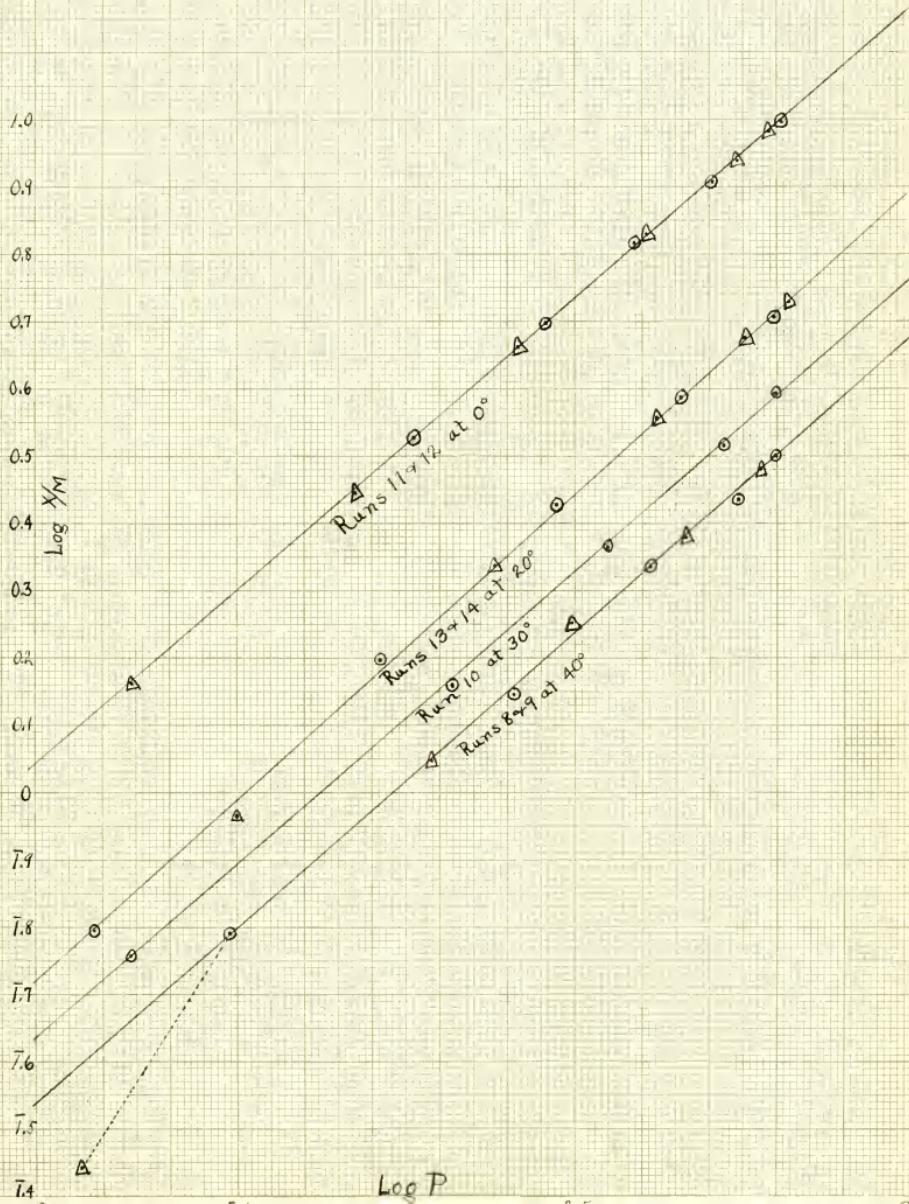
DISCUSSION OF RESULTS

The results given in Table I are pictured graphically in Figs. I and II, which show the applicability of Freundlich's isotherm. This equation is $X/M = \alpha \, P^{1/n}$, in which X/M and P have the meanings given above, α and $\frac{1}{n}$ being constants. The values of X/M are plotted against P in Fig. I, and it will be observed how these curves differ from the parabolic type usually obtained, in that these approximate straight lines except in the vicinity of the origin. Expressing Freundlich's equation logarithmically, we have:

$$\log X/M = \log \alpha + \frac{1}{n} \log P$$

Hence if $\log X/M$ is plotted against $\log P$, straight lines should result, as is shown to be the case in Fig. II.

It will be noted in these curves that $\frac{1}{n}$, which expresses the slope of the curve, is practically the same for all four temperatures, while X, the amount taken up when $P = 1$, or the intercept on the YY' axis, increases as the temperature falls.

In order to apply our ideas of capillary effects, Table II has been arranged, preparatory to the use of the equation

$$V = K \, (P\,\sigma/P_0)^{1/n}$$

in which the symbols have the meanings given on page 4. To find V, Lord Rayleigh's value of the density of gaseous CO_2 (1.9652 g. per liter at C^0 and 760 mm.) and Amagat's values

for that of liquid CO_2 are taken. Then $\dfrac{0.0019652 \, X}{M}$ divided by Amagat's values of the density of the liquid (Landolt-Börnstein's Tables) transforms $1/M$ into V. P is the pressure measured, P_o is the condensation pressure taken from Regnault's values in Landolt-Börnstein, and σ is read from a curve based upon data of Verschaffelt, given also in Landolt-Börnstein. From his values of σ at -24.3^o, 8.9^o, 15.2^o and 20.9^o a curve is drawn and the values of σ at 0° and at 20° are read from this. This seems preferable to making use of such a relationship as that of Ramsey-Eötvos-Shields, since the temperature is so near the critical point. Even this graph becomes value-less at 30°, and so no attempt was made to draw a curve at that temperature, and of course not at 40°, where σ, P_o and D are all unknown.

TABLE II

Run No. 11

Temp. $0°$; $P_0 = 26904$ mm.; $\sigma = 4.6$ $D = 0.914$

x/m	V	log V	log P/P_0	log P σ/P_0
3.37	0.00725	$\bar{3}.86051$	$\bar{3}.83052$	$\bar{2}.49528$
4.98	0.01071	$\bar{2}.02989$	$\bar{2}.02525$	$\bar{2}.68801$
6.54	0.01406	$\bar{2}.14788$	$\bar{2}.15812$	$\bar{2}.82088$
8.10	0.01742	$\bar{2}.24104$	$\bar{2}.27488$	$\bar{2}.93764$
9.94	0.02137	$\bar{2}.32977$	$\bar{2}.37658$	$\bar{1}.03914$

Run No. 12

Temp. $0°$; $P_0 = 26904$ mm.; $\sigma = 4.6$ $D = 0.914$

x/m	V	log V	log P/P_0	log P σ/P_0
1.45	0.00312	$\bar{3}.49379$	$\bar{3}.41417$	$\bar{2}.07693$
2.79	0.00599	$\bar{3}.77737$	$\bar{3}.74593$	$\bar{2}.40869$
4.60	0.00988	$\bar{3}.99481$	$\bar{3}.98480$	$\bar{2}.64756$
6.75	0.01451	$\bar{2}.16167$	$\bar{2}.17614$	$\bar{2}.83890$
8.69	0.01869	$\bar{2}.27151$	$\bar{2}.31110$	$\bar{2}.97086$
9.60	0.02063	$\bar{2}.31453$	$\bar{2}.35895$	$\bar{1}.02171$

Run No. 13

Temp. 20°; $P_0 = 44718$ mm.; $\sigma = 1.10$ D = .766

x/M	V	log V	log P/P_0	log $P\sigma/P_0$
0.62	0.00160	$\bar{3}.20429$	$\bar{3}.13684$	$\bar{3}.17823$
1.57	0.00404	$\bar{3}.60588$	$\bar{3}.56120$	$\bar{3}.60259$
2.69	0.00690	$\bar{3}.83875$	$\bar{3}.82274$	$\bar{3}.86413$
3.88	0.00996	$\bar{3}.99845$	$\bar{2}.00910$	$\bar{2}.05049$
5.08	0.01303	$\bar{2}.11496$	$\bar{2}.14486$	$\bar{2}.18625$

Run No. 14

Temp. 20°; $P_0 = 44718$ mm.; $\sigma = 1.10$ D = .766

x/M	V	log V	log P/P_0	log $P\sigma/P_0$
0.92	0.00237	$\bar{3}.37422$	$\bar{3}.35056$	$\bar{3}.39195$
2.17	0.00557	$\bar{3}.74573$	$\bar{3}.73014$	$\bar{3}.77153$
3.62	0.00929	$\bar{3}.96793$	$\bar{3}.97099$	$\bar{2}.01328$
4.76	0.01222	$\bar{2}.08703$	$\bar{2}.10344$	$\bar{2}.14483$
5.36	0.01375	$\bar{2}.13836$	$\bar{2}.16835$	$\bar{2}.20974$

Run No. 10

Temp. 30°; P_0 = 56118 mm.; σ unknown   D = .590

x/m	V	log V	$\log P/P_0$	$\log P \sigma/P_0$
0.57	0.00187	$\bar{3}$.27258	$\bar{3}$.09176	_____
1.44	0.00475	$\bar{3}$.67627	$\bar{3}$.56972	_____
2.31	0.00759	$\bar{3}$.88004	$\bar{2}$.80071	_____
3.27	0.01074	$\bar{2}$.03099	$\bar{3}$.97116	_____
3.91	0.01286	$\bar{2}$.10933	$\bar{2}$.04742	_____

Fig III
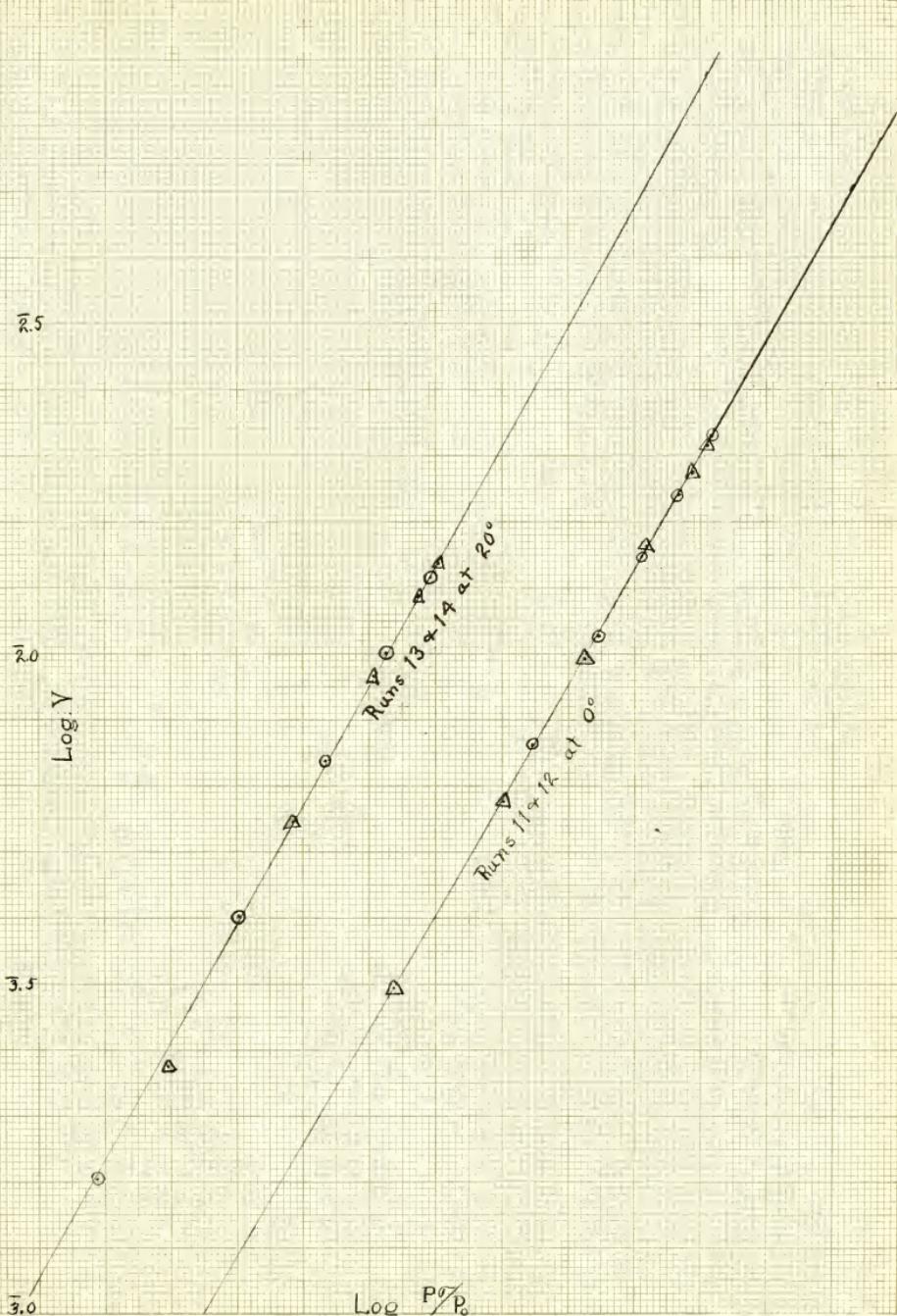
In Fig. 3 are plotted the values of $\log V$ and $\log \frac{P \sigma}{P_0}$ found in Table II. Here we note a feature characteristic of CO_2 and at marked variance with the conduct of SO_2, NH_3 and butane. In each of these latter cases, it was found that, when $\log V$ was plotted against $\log \frac{P \sigma}{P_0}$, the curves for all temperatures became identical, while in the case of CO_2 this is not at all true; the curves run practically parallel, indicating that $1/n$ for both temperatures is the same, but K at 0° is widely different from K at 20°. In fact, evaluation of these constants, either by solving simultaneously the equations for pairs of points, or by direct readings from a graph plotted on uniform scale, gives a value to $1/n$ at 0° of 0.865 and at 20° of 0.898, corresponding to a variation of only about one degree in the slope, while K at 0° is 0.1456 and K at 20° is 0.5585.

In the case of carbon dioxide it is, therefore, evident that the constant K is not independent of the temperature in the neighborhood of the critical temperature, but increases with increasing temperature. This behavior may be accounted for provided our evaluation of the corresponding pressure $(P \sigma/P_0)$ is erroneous. It is evident that low values of surface tension at the higher temperatures would produce an effect similar to that found in the case of carbon dioxide at 0° and

20°. We are therefore forced to postulate that the surface tension of a liquid in a capillary tube is subject to variations which hitherto have not been taken into account. In all applications of capillarity the surface tension has been regarded as being constant, varying only with the temperature, but there is considerable evidence that can be utilized to show the necessity of a variation in surface tension produced by factors other than this. For example, the empirical formula itself

$$V = K \left(P/P_0^{\sigma} \right)^{1/n}$$

which contains σ raised to a fractional power, expresses the physical fact that the surface tension operates more strongly in the initial stages of adsorption, when according to our theory the radii of the active portions of the pores are small.

Furthermore, it is reasonable to assume that the surface tension is a function of the composition of the vapor phase. In the case of a plane liquid surface the vapor pressure can only be varied by a change of temperature, but with a liquid in a capillary tube of varying diameter it is possible to change over a wide range the composition of the vapor in equilibrium with the liquid. Thus, for example, it is unreasonable to suppose that liquid CO_2 at 20° under a vapor pressure of 4472 cm. possesses the same surface tension as does liquid CO_2 in a capillary tube of such dimensions that the equilibrium pressure is

only 10 cm.

In the case of sulphur dioxide, ammonia and butane it was found that the value of K was constant over the temperature range studied, but it is to be noted that in no case were the measurements extended higher than 30° below the critical temperature. From these facts we may infer that the change in surface tension with the composition of the vapor phase becomes a most important factor in the neighborhood of the critical temperature. This is in agreement with the well-known instability of the meniscus near this point, in which vicinity it becomes impossible to measure surface tension by the customary methods. Very slight changes in conditions then, produce very large changes in its value; it becomes an excessively sensitive quantity; the temperature coefficients of both surface tension and density become unusually high in this neighborhood.

A rough qualitative idea of the change in surface tension in the capillaries can be obtained by extrapolation to 30° from the values of K, and $1/n$ at 0° and 20°. At 0° $K = 0.1456$, and at 20° $K = 0.5585$. If we assume the same rate of change between 20° and 30° as between 0° and 20° (probably the rate increases, but this is uncertain ground), then at 30° K would be 0.765. Similarly $1/n$ would be 0.914 at 30°. Substituting these values in the equation $V = K(P^{\sigma}/P_0)^{1/n}$ we

can solve for σ in the pores of the gel. This comes out
to be 1.02. If we assume that the value of K does not change
between 20° and 30° and make the same substitutions, we ob-
tain a value of 1.32 dynes for σ. As mentioned above,
however, it is likely that K does continue to change between
20° and 30°, and so the above can be considered only as a
rough approximation, which is given only to indicate that there
is an increase in σ. At 30°, only 1° below the critical tem-
perature, the surface tension of liquid CO_2 showing a plane
surface would be infinitessimally small. We may then infer
from this rough calculation that the surface tension in the
pores of the gel actually is raised, and that at 30° its value
lies somewhat above unity.

A sounder method theoretically of arriving at the same
conclusion will now be given, which, altho more tedious, is
also more trustworthy. The following relationship has been
established for the lowering of the vapor pressure in a capil-
lary tube:

$$\ln P_0/P = \frac{2}{r} \frac{\sigma}{D_l} \frac{M}{RT}$$

in which M is the molecular weight of the gas, D_l the den-
sity of the liquid, r the radius of the capillary, R the gas
constant, σ the surface tension at the temperature T, P_0
the ordinary vapor pressure of the liquid and P the pressure
actually existing in the capillary. Using this formula it is

Fig. IV

Runs 11 & 12 at 0°

V in cc.

.020

.015

.010

.005

0
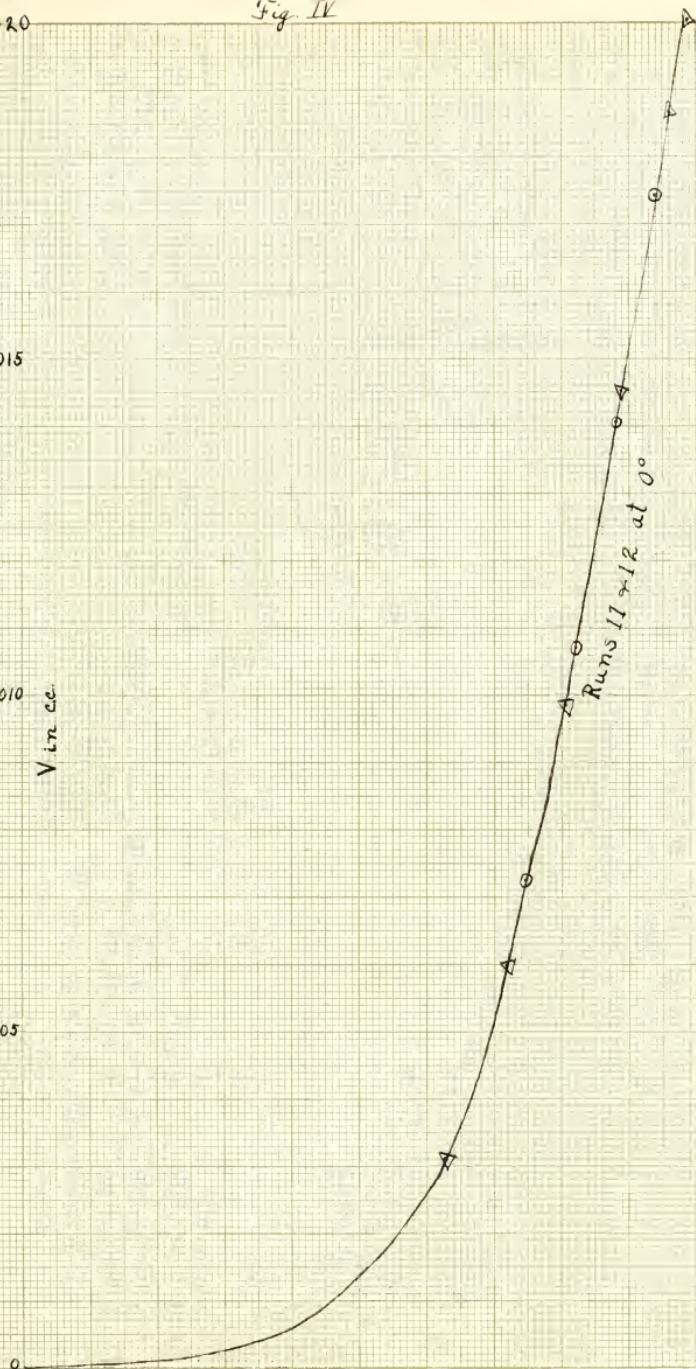
possible to obtain values of r at the measured pressures, P,
of a gas at temperatures sufficiently far below the critical
temperature for the effect of capillarity upon surface tension
to be negligible. Having done this, the values of V corres-
ponding to the pressures P can be plotted in the form of a
curve. This has been done in Fig. 4, using the 0° runs with
CO_2. The temperature of these runs is not as low as could
be desired, as even at 0° it is possible that the value of σ
as taken from measurements made by the ordinary methods may be
lower than the value actually existing in the capillaries; but
an increase in σ at 0° would increase the effect which is to
be mentioned later, and would thus strengthen rather than weak-
en the reasoning upon which we base our conclusions. We there-
fore make the assumption (which we consider a conservative one)
that the surface tension at 0° remains unchanged or but inap-
preciably changed in the capillaries, and calculate r for the
pressures measured in these runs. Then we plot these values
of r, expressed in $\mu\mu$, against the values of V correspond-
ing to these same pressures. This gives a smooth curve re-
lating the radius of the pore to the volume of liquid held up
to that point. A consideration of the probable conical shape
of the pores will make clear how there can be this variation
in r as V changes.

Our next step is to take the values of V found at 30°, read
from the curve of Fig. 4 the values of r corresponding to these

volumes, and substitute these values in the same equation
given above, except that in this case σ is the unknown and
we solve for it. When this is done we obtain the noteworthy
value of 3.45 dynes for σ at 30°. When the same procedure
is carried out for the runs at 20°, the values of σ obtained
are all slightly above 4 dynes, the mean being 4.08. This is
as expected; capillary forces raise σ in each case above the
normal value (at 30° σ cannot be said to have a "normal" value,
the meniscus at this temperature being too unstable to permit
measurements being made). It will be noted that this conclu-
sion is in harmony with that arrived at on page 25, namely that
a meniscus and surface tension phenomena actually exist at these
(relatively) high temperatures, that capillary forces are ef-
fective in raising surface tension, and that this rise is more
noticeable in the case of liquids near their critical tempera-
ture, in which condition the surface tension is far more sensi-
tive to changes in conditions. The conclusion drawn on page 25
was based upon rough approximations of the value of M, and it
is not surprising that the value of σ at 30° based on such
data should not agree with that found by the more careful con-
sideration of the radii of the pores, but the important fea-
ture is the fact that both lines of reasoning lead to the same
conclusion qualitatively. Even in this latter case, as noted
before, the assumption that the surface tension at 0° is un-
changed or negligeably changed by capillary forces may be

ultra-conservative; but if surface tension at 0° is actually increased, we should obtain yet higher values for it at 20° and 30°, showing that the capillary effect is even greater than indicated by the figures given above.

If we substitute this corrected value of 4.08 for σ at 20° in the formula $V = K(P^{\sigma}/P_0)^{1/n}$, and plot log V against log P^{σ}/P_0 as was done in Fig. 3, we find that the lines for 0° and 20°, instead of being widely separated as in Fig. 3 now practically coincide as shown in Fig. 5, K becoming the same for both temperatures as demanded by theory. This means that with CO_2, as with SO_2, NH_3 and butane, the same volume is taken up at corresponding pressures, but that, in the case of CO_2 near the critical temperature, this fact is masked in the calculations by the increase in surface tension above normal. If the corrected values of σ at 30° are substituted in the formula and the results plotted logarithmically as in Fig. 5, the curve obtained does not coincide with that for 0° and 20° as would be desired, but falls a little above. The difference is quite appreciable, but it must be noted that the sample of gel used for the 30° work was different from that used in the 0° and 20° runs, and this fact alone would account for a difference in K. There is also the uncertainty as to the true density in the pores at this temperature, due to the dilation effect mentioned on page 7, and the conservative assumption that at 0° the gas is far enough below its critical

$$V = \eta \left(\frac{V_0 \sigma}{\sigma_0} \right)^2$$

$$V = \eta \sigma^{\frac{1}{m}}$$

Fig V
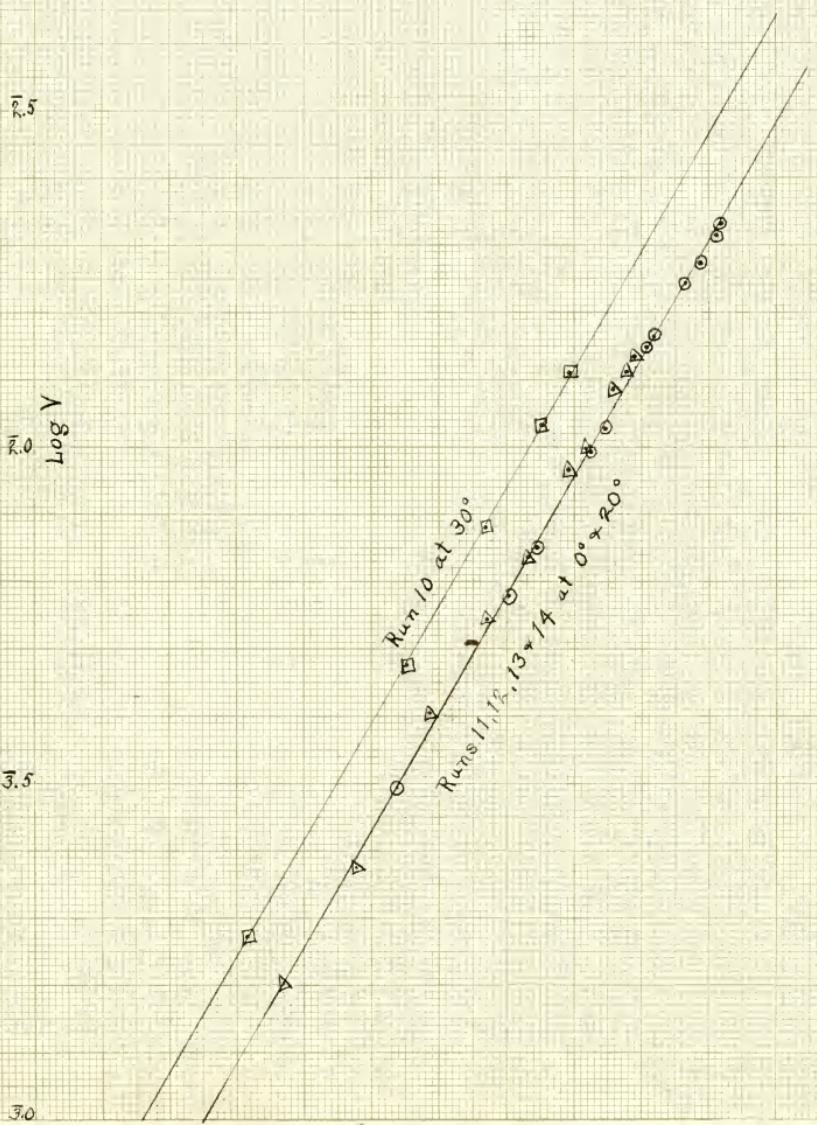
temperature to permit taking the 0^0 curve as a reference. We can then say that the proposed capillary effect on surface tension near the critical temperature explains quantitatively the variation of the 20^0 runs from those at 0^0 and brings the 50^0 run very nearly into accord.

Since, then, capillarity lowers the vapor pressure in a capillary and increases surface tension, and since there is no perceptible break in the adsorption phenomena between 30^0 and 40^0, we think that there is justification for extending the capillary condensation theory of adsorption to temperatures above the ordinary critical temperature, and propose the idea that in the pores of the gel the critical temperature is raised, that condensation and surface tension exist even at 40^0 in the case of CO_2. Since we know neither the density nor vapor pressure that the condensed phase would have at this temperature, no attempt has been made to calculate the surface tension nor to subject the results of the 40^0 runs to the same mathematical treatment as the others. We do know, however, that the vapor pressure is lowered, so it cannot be objected that we are postulating the existence of a liquid of less density than its saturated vapor.

SUMMARY

1.   Accurate measurements have been made of the adsorption of carbon dioxide by silica gel at 0°, 20°, 30° and 40° at pressures below one atmosphere.

2.   When the equation $V = K(P^{\sigma}/P_0)^{1/n}$ was applied to the experimental results, it was found that K at 0° was not equal to K at 20°, as had been true of K at different temperatures in the case of other gases to which the capillary theory of adsorption had been applied. The explanation is offered that this is due to an increase in surface tension at temperatures near the critical temperature, brought about by capillary forces. This conclusion has been verified by applying the formula

$$\ln {}^{P_0}/_P = \frac{2 \sigma K}{r D_\ell RT}$$

to the results at low temperatures, calculating the values of r corresponding to different internal volumes, then using the internal volume values obtained at the higher temperatures to calculate surface tension at these higher temperatures. The results indicate an increase in surface tension. The corrected surface tensions result in making K at 0° equal to K at 20°, and a not greatly differing value for K at 30°.

3.   The capillary condensation theory has been extended to temperatures above the critical temperature, it being proposed that the latter is raised in the pores of the adsorbent.

BIOGRAPHY

Walter Creigh Preston was born November 3, 1895 at
Lewisburg, W. Va. He received his preparatory education
at the Greenbrier Presbyterial Military School of that
town, and entered Washington and Lee University in the fall
of 1912. He received the degree of B. A. from that insti-
tution in 1915, and then engaged in teaching for three years
in the high schools of his native state and at Augusta
Military Academy of Virginia. He enlisted in the United
States Army in 1918, serving until the end of the war, after
which he taught at McGuire's University School of Richmond,
Va. During 1919-1920, while teaching at Mt. Vernon College
of Baltimore, he was enrolled as a special student at Johns
Hopkins University, and has been a full-time graduate student
during 1920-21, 1921-22, 1922-23, majoring in Chemistry, with
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ordinate subjects.